

FORM PTO 1390 (REV 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER DNAG 227 - PFF/JRC
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 09/980182
INTERNATIONAL APPLICATION NO. PCT/EP00/05122	INTERNATIONAL FILING DATE 5 June 2000	PRIORITY DATE CLAIMED 4 June 1999	
TITLE OF INVENTION COATING METHODS AND COATING MIXTURE			
APPLICANT(S) FOR DO/EO/US Georg GROS,			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing 35 U.S.C. 371 3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371 (f)). The submission must include items (5), (6), (9) and (21) indicated below. 4. <input type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (PCT Article 31). 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c)(2)) <ol style="list-style-type: none"> a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). b. <input checked="" type="checkbox"/> has been communicated by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371 (c)(2)). <ol style="list-style-type: none"> a. <input checked="" type="checkbox"/> is attached hereto. b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). 7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). b. <input checked="" type="checkbox"/> have been communicated by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. 8. <input checked="" type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)). 9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)). 10. <input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)). 			
Items 11 to 20 below concern document(s) or information included:			
<ol style="list-style-type: none"> 11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. 14. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 15. <input type="checkbox"/> A substitute specification. 16. <input type="checkbox"/> A change of power of attorney and/or address letter. 17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825. 18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). 19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). 20. <input type="checkbox"/> Other items or information: PCT/IPEA/416; PCT/ISA/210 			

U.S. APPLICATION NO. (if known) 09/980182 INTERNATIONAL APPLICATION NO. PCT/EP00/05122	ATTORNEY'S DOCKET NUMBER DNAG 227-PFF/JRC				
17. <input checked="" type="checkbox"/> The following fees are submitted:					
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)): <input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1040.00 <input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$890.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$740.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$710.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00					
ENTER APPROPRIATE BASIC FEE AMOUNT =					
Surcharge of \$ <u>130.00</u> for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).					
CLAIMS	NUMBER FILED				
Total claims	15-20 =				
Independent claims	1-3 =				
MULTIPLE DEPENDENT CLAIM(s) (if applicable)					
NUMBER EXTRA	RATE				
0	X				
1	X				
TOTAL OF ABOVE CALCULATIONS =					
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.					
SUBTOTAL =					
Processing fee of \$ _____ for furnishing the English translation later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). +					
TOTAL NATIONAL FEE =					
Fee for recording the enclosed assignment (37 CFR 1.21 (h)). Assignment Must be accompanied by appropriate cover sheet (37 CFR 3.28, 3.31) (_____ per property). +					
TOTAL FEES ENCLOSED =					
<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 80%; text-align: right;">Amount to be Refunded:</td> <td style="width: 20%; text-align: center;">\$</td> </tr> <tr> <td style="text-align: right;">Charged:</td> <td style="text-align: center;">\$</td> </tr> </table>		Amount to be Refunded:	\$	Charged:	\$
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Charged:	\$				
a. <input checked="" type="checkbox"/> A check in the amount of \$ <u>1020.00</u> to cover the above fees is enclosed.					
b. <input type="checkbox"/> Please charge my Deposit Account No. <u>50-0624</u> in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.					
c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required or credit Any overpayment to my Deposit Account No. <u>50-0624</u> . A duplicate copy of this sheet is enclosed.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO: James R. Crawford FULBRIGHT & JAWORSKI L.L.P. 666 Fifth Avenue New York, New York 10103 (212) 318-3148 Customer No. 24972					
SIGNATURE: <u>James R. Crawford</u> NAME: _____					
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s) : Georg GROS.
Based on: : PCT/EP00/05122
International Filing : June 5, 2000
Date
For : COATING METHOD AND COATING MIXTURE

Hon. Commissioner of Patents
and Trademarks
Washington, D.C. 20231

November 29, 2001

PRELIMINARY AMENDMENT

Sir:

Prior to prosecution, please amend the above-identified patent application as follows:

IN THE CLAIMS:

Cancel claims 1-15 without prejudice and substitute the following claims:

16. A coating mixture with anticorrosive properties, comprising a polymeric organic binder, a low-molecular liquid compound to be subjected to free-radical polymerization, a compound forming radicals under the influence of actinic radiation, and a conductive inorganic pigment, from the group including oxides, phosphates and phosphides of iron and aluminum and graphitemica pigments.
17. The mixture as claimed in claim 16, wherein the conductive inorganic pigment is magnetizable iron oxide or iron phosphide or a combination of these two pigments.
18. The mixture as claimed in claim 16, wherein the binder is present is an amount of 15 to 60, preferably 20 to 50, in particular 20 to 40% by weight,

the polymerizable compound is present in an amount of 24 to 60, preferably 20 to 55, in particular 25 to 50% by weight,

the pigment is present in an amount of 10 to 40, preferably 10 to 35, in particular 12 to 35% by weight,

and the photoinitiator is present in an amount of 5 to 30, preferably 8 to 25, in particular 8 to 20% by weight, as well as further additives are present in an amount of 0.1 to 5, preferably 0.3 to 4, particularly preferably 0.4 to 3% by weight.

19. The mixture as claimed in claim 16, wherein it is free of organic solvents and water.
20. The mixture as claimed in 16, wherein the binder itself still contains polymerizable groups.
21. The mixture as claimed in 16, wherein the binder is selected from the group selected from the group consisting of condensation resins, epoxy resins, poly(meth)acrylates, polyurethanes, polyesters and polyethers, preferably epoxidized novolaks, bisphenol epichlorohydrin condensation products and esterification products of these resins or polymers with (meth)acrylic acid.
22. The mixture as claimed in claim 16, wherein the compound to be subjected to free-radical polymerization is a mixture of compounds, at least part of which contains more than one polymerizable group in the molecule or completely consists of the same.

23. The mixture as claimed in claim 22, wherein the compound to be subjected to free-radical polymerization is an ester of an α,β -unsaturated carboxylic acid, preferably acrylic or methacrylic acid, with a divalent or polyvalent monomeric or oligomeric alcohol.
24. The mixture as claimed in claim 23, wherein the compound to be subjected to free-radical polymerization is selected from the group including dipropylene and tripropylene glycol di(meth)acrylate, 2-acetoacetyloxy ethyl methacrylate, hexanediol diacrylate, hydroxypropyl methacrylate, hydroxyethyl methacrylate and trimethylolpropane triacrylate.
25. The mixture as claimed in claim 16, wherein the compound forming radicals upon irradiation is an aromatic keto compound.
26. A method of applying a slidable anticorrosive layer to a metallic substrate, characterized in that a mixture as claimed in claim 16, is applied to the surface of a metallic substrate and the coating applied is irradiated with actinic radiation of such an intensity and for such a period that a firm, hard, tough, corrosion-resistant layer is formed.
27. The method as claimed in claim 26, wherein the coating mixture is applied to obtain a layer thickness of 2 to 8 μm , preferably 3 to 7 μm .
28. The method as claimed in claim 26, wherein the substrate to be coated is a steel sheet which has previously been zinc-coated and/or chromated or has been pretreated free of chromate.

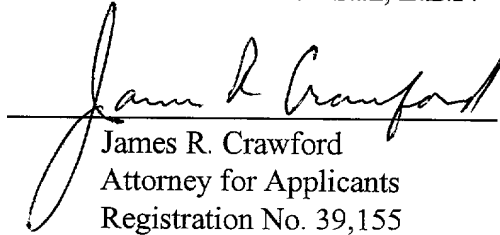
29. The method as claimed in claim 25, wherein that coating and curing are effected continuously one after the other in one step and the layer cured by radiation is possibly postcured thermally.
30. A flexible metal sheet which is electrolytically zinc-coated or hot-dip coated and/or chromitized or pretreated free of chromate and has an organic layer applied thereto, which layer can be obtained by the method as claimed in claim 26.

REMARKS

The purpose of this amendment is to conform the claims to standard U.S. practice.

Respectfully submitted,

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Coating Method and Coating Mixture

This invention relates to a method of applying a weldable anticorrosive coating to a metallic substrate, in particular a body sheet for the automotive industry, as well as a coating mixture for performing this method.

Weldable protective coatings as mentioned above on the basis of inorganic pigment particles and organic polymers are known and described for instance in DE-C-34 12 234.

EP-B-298 409 describes such coatings for steel sheet, which coatings have a layer of silicic acid and a cured organic matrix, which was obtained from an epoxy resin and a polyvalent isocyanate by thermal cross-linkage.

EP-C-344 129 describes similar coatings, which are obtained by curing epoxy resins by means of amines, melamines, phenol resins and the like.

EP-A-761 320 describes coated steel sheets, which carry an organic protective layer which was produced from an aqueous solution by electrolytic polymerization of ionogenic polymerizable organic compounds.

EP-A-659 855 describes an aqueous coating mixture, from which curable antirust coatings can be deposited.

All these known coating mixtures contain organic or aqueous solvents, which must be evaporated upon application. To achieve a durable resistance to chemicals and weathering influences as well as a sufficient rust protection, these coatings must be cured by heating. This has the disadvantage of a higher consumption of energy and the risk of the emission of volatile components to the environment by evaporation. Moreover, chemically cross-linked polymer coatings frequently tend to become brittle.

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This means that the steel sheets provided with a thermally cured organic coating in the known manner are deformable only to a limited extent, for instance by deep-drawing or bevelling. In most cases, this requires a pretreatment with drawing oil. The required high curing temperatures can lead to structural changes in the substrate.

The known coating mixtures frequently contain zinc powder. Such mixtures tend to corrosion, which starts between the pigmented layer and the metallic, possibly zinc-coated substrate. On the other hand, a content of conductive components is required to achieve a weldable coating.

It was the object of the invention to provide a coating mixture and a coating method for corrodible metallic substrates, which provide a corrosion- and solvent-resistant slidable weldable coating which can be deformed together with the substrate without being damaged.

The invention proceeds from a mixture for applying an anticorrosive layer to a metallic substrate, comprising a polymeric organic binder, a low-molecular liquid compound to be subjected to free-radical polymerization, a compound forming radicals under the influence of actinic radiation, and a conductive pigment.

In accordance with the invention, there is furthermore proposed a coating method for a metallic substrate, which method is characterized in that the aforementioned mixture is applied to the surface of the substrate and the coating applied is irradiated with actinic radiation for such a period and with such an intensity that a firm, hard, tough corrosion-resistant layer is formed.

Actinic radiation is understood to be such radiation whose energy is sufficient for activating the polymerization initiator. Normally, it should at least have the energy or the frequency of visible light; short-wave visible or ultraviolet light is preferred. Naturally, any radiation of a shorter wavelength, and thus of a higher energy, can likewise be used. For instance, electron radiation may be used as well, which has the advantage that no photoinitiator is required.

The inventive coating mixture preferably is free of inert volatile solvents, in particular organic solvents or water.

The polymeric binder is solid and may be saturated itself. Preferably, the polymeric binder contains unsaturated polymerizable groups which in the case of the radiation-initiated polymerization of the polymerizable compound can react with the same and form an insoluble network.

Suitable binders include condensation resins, epoxy resins, poly(meth)acrylates, polyurethanes, polyesters, polyethers and other similar polymers or polymers derived therefrom. Preferred binders include epoxidized novolaks, bisphenol epichlorohydrin condensation products and esterification products of the above-mentioned resins or polymers with acrylic or methacrylic acid. When epoxidized novolaks are used, the same may be made on the basis of phenol, substituted phenols (for instance cresol) or also polyvalent, possibly substituted phenols or mixtures of the aforementioned phenols.

The low-molecular monomeric compound contains at least one polymerizable ethylenically unsaturated group. To achieve a rather good cross-linkage and thus insolubility and resistance of the layer to solvents, chemicals and weathering influences, at least part of the polymerizable compounds should contain at least two polymerizable groups. Preferably, the polymerizable compound is an ester of an α,β -unsaturated carboxylic acid with a di- or polyvalent, possibly also oligomeric alcohol. Esters of acrylic or methacrylic acid are preferred particularly. Apart from ester groups, the polymerizable compounds may also contain other functional groups, in particular ether, amide or urethane groups. Examples for suitable polymerizable compounds include dipropylene and tripropylene glycol di(meth)acrylate, 2-acetoacetyloxy ethyl methacrylate, hexanediol diacrylate, hydroxypropyl methacrylate, hydroxyethyl methacrylate, trimethylolpropane triacrylate.

As compounds forming radicals when irradiated, in particular photoinitiators, especially those can be used, which have a strong absorption in the spectral range of the radiation used, in particular of the near ultraviolet or short-wave visible light, i.e. with a wavelength approximately in the range from 180 to 700 nm. There can be used above all aromatic carbonyl compounds and the derivatives thereof, such as quinones, ketones and the ketals thereof, for example benzildimethylketal, benzoin, substituted benzoin and benzoin ethers, α -amino ketones; furthermore polynuclear heterocyclic compounds such as acridines, phenazines and the sub-

stitution products thereof as well as substituted phosphine oxides, for instance bisacyl phosphine oxides.

To prevent a premature polymerization of the coating mixtures, the same normally contain small amounts of polymerization inhibitors, for instance hydroquinone and the derivatives thereof and tert-butyl phenols. Normally, such inhibitors are already included in all commercially available polymerizable compounds.

Normally, the mixtures furthermore contain coating aids, for instance surface-active substances, in particular polysiloxanes, silanes and silicon-free oligomeric or polymeric surfactants. They can furthermore contain adhesion promoters, soluble corrosion inhibitors, dyes and color pigments.

Another important component are inorganic pigments, in particular anticorrosive or antirust pigments, for instance oxides, phosphides or phosphates of iron or aluminum, and other conductive pigments, for instance graphite-mica pigments.

The amounts of the components of the coating mixture lie within the following ranges:

Binder: generally 15 to 60, preferably 20 to 50, in particular 20 to 40 % by weight.

Polymerizable compound: generally 20 to 60, preferably 20 to 55, in particular 25 to 50 % by weight.

Pigment: generally 10 to 40, preferably 10 to 35, in particular 12 to 35 % by weight.

Photoinitiator: generally 5 to 30, preferably 8 to 25, in particular 8 to 20 % by weight.

Additives: generally 0.1 to 5, preferably 0.3 to 4, particularly preferably 0.4 to 3 % by weight.

The coating mixtures are generally prepared by grinding the insoluble pigment particles together with the remaining soluble components to obtain a homogeneous viscous mass. The viscosity should lie in a range which allows a uniform application to form a thin layer having a thickness of about 2 to 8 μm . The viscosity can be adjusted by choosing the kind and quantity above all of the binder and of the polymerizable compound. In general, it lies in the range from 1000 to 10000 mPas.

The metallic substrate to be coated preferably is a strip or sheet which mostly consists of steel and has a thickness in the range from about 0.2 to 1.6 mm. Normally, the strip surface is electrolytically or hot-dip zinc-coated and/or chromatised or subjected to a similar pretreatment. To the surface pretreated in this way, the weldable coating in accordance with the invention is then applied. In general, the strip or sheet is unwound onto rolls, so-called coils. To apply the inventive coating, the coil is wound off, and upon coating is wound up again. Application is expediently effected in a continuous process, in which the strip runs through a coating station and thereafter through a curing station. Coating can be effected by spraying, by means of slot nozzles or by means of rollers. Roller coating is preferred in general. Coating is preferably effected at room temperature or a temperature slightly above room temperature, i.e. at temperatures in the range from about 20 to 40°C, the material and the substrate preferably having a temperature of 40 to 50°C. The layer thickness can generally be 2 to 8, preferably 3 to 7 μm . Since the coating compound preferably is free of solvent, this corresponds substantially to the layer thickness of the cured layer.

Upon coating, curing is effected, advantageously by passing through a curing station. In an inert gas atmosphere, for instance under nitrogen, and at a distance of few centimeters, the strip is passed below a radiation source which corresponds to the entire width of the strip. The strip speed depends on the layer thickness, the light sensitivity of the layer, the lamp distance and the lamp performance. It furthermore depends on whether irradiation is effected in air or in nitrogen. If desired, it can be accelerated by providing two or more radiation sources disposed one behind the other. As radiation sources, UV light sources such as gas discharge lamps, xenon lamps or sodium vapor lamps are preferably used, which have emission maxima in the spectral range from about 100 to 700 nm, in particular in the range from 200 to 600 nm. Lamps substantially emitting in the short-wave visible range from about 400 to 550 nm can also be used. In principle, radiation of higher energy, for instance electron radiation, can also be used for curing. Irradiation, like coating, is effected at ambient temperatures, which do not lie much above room temperature, i.e. in general not above about 50°C. The irradiated layer surface reaches temperatures up to about 80°C. If an additional postcure is desired, the same can be effected by a subsequent brief passage through a drying oven, which has a temperature up to about 250°C, and the surface temperature of the strip can reach about 150 to 160°C with a dwell time of 30 seconds. In this way,

the corrosion resistance can still be increased; however, such postcure is generally not required.

In any case, the layer composition and the curing conditions should be chosen such that a hard, firm, corrosion-resistant layer is obtained, which is, however, sufficiently tough, so that a deformation of the substrate, for instance of the steel sheet, is ensured without brittle cracks in the anticorrosive layer.

The processing of the anticorrosive layer by the inventive method provides for a wide variation of the layer thickness within the range indicated above. The layer adheres to the substrate firmly and durably; it can be overpainted as usual, for instance by cationic dip-coating, and has a smooth, slidable surface. With a thickness of the cured layer of 3 μm , up to 900 welding spots per electrode are achieved.

In the main field of application of the inventive method, the production and processing of body sheets for the automotive industry, the inventive coating of the sheets (coils) is advantageously effected at the sheet manufacturer after the pretreatment. The sheets are then protected against corrosion ("coil-coated steel") and in this stage can be transported to the finisher, in general to the car manufacturer, and be stored. They are deformed as desired and subjected to a usual dip-coating as priming. To this prime coat, a finishing paint will then be applied at a later date. In general, the prime coat cannot reach all parts of the deformed steel sheet. Due to the inventive coating, the surface still remains protected against corrosion despite deforming and welding.

In the following examples, preferred embodiments of the inventive method are explained. Amounts and ratios are understood to be in weight units, unless otherwise indicated. The amounts are usually indicated in parts by weight (pbw).

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Example 1

A mixture of

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|------|-----|---|
| 20 | pbw | of a novolak epoxy resin esterified with acrylic acid (Viaktin® VTE 6152, 65 % in tripropylene glycol diacrylate, Vianova Resins), |
| 15 | pbw | of an aliphatic urethane acrylate (Syntholux® DRB 227, 65 % in hydroxypropyl methacrylate, Synthopol-Chemie), |
| 26.7 | pbw | acetoacetyloxy ethyl methacrylate (Lonzamon® AAEMA, Lonza AG, Basel), |
| 8 | pbw | magnetizable iron oxide (Magnetschwarz® S 0045, BASF AG), |
| 12 | pbw | iron phosphide (Ferrophos® HRS 2132, Occidental Chemical Corp., Niagara, USA), |
| 3 | pbw | aluminum triphosphate (K-White 105, Teikoku Kako Co., Osaka), |
| 6 | pbw | benzildimethylketal (Irgacure® 651, Ciba-Geigy AG), |
| 1 | pbw | Irgacure® 1850 (Ciba-Geigy), mixture of 50 % 1-hydroxy-cyclohexyl-phenyl ketone and 50 % bis(2,6-dimethoxybenzoyl-2,4,4-trimethylpentyl-phosphine oxide), |
| 8 | pbw | 1-hydroxy-cyclohexyl-phenyl ketone (Irgacure® 184), and |
| 0.3 | pbw | substituted phosphine oxide (Irgacure® 819) |

was thoroughly ground on a roller mill for two hours, until a homogeneous viscous mixture was obtained. The viscosity was 100 s outflow time from a flow cup in accordance with European standard EN ISO 2431 (CEN). In a roller coating device, with a rate of passage of 20 m/min, the mixture was applied to a degreased and dried sheet of electrolytically zinc-coated and chromatized steel with a thickness of 0.8 mm and a width of 20 cm, such that a coating with a thickness of 3 μm (4 g/m²) was obtained. Directly thereafter, the sheet was passed through a curing zone, where it was irradiated at a distance of 8 cm by means of two succeeding UV gas discharge lamps of the firm IST, type CK-1 (gallium-doped) and CK (mercury-doped), each with a performance of 160 W/cm and emission maxima in the range from 200 to 600 nm under a nitrogen atmosphere with 3000 ppm residual oxygen, the surface temperature of the coating maximally reaching 80°C. The cured coating was resistant to butanone; when bevelling the coated sheet by an angle of 90°, the sheet showed no signs of damages or cracks in the anticorrosive layer. The layer surface was smooth and slidable. Even after 360 hours salt spray test according to DIN 50021 it was still undamaged and showed no signs of red rust.

Example 2

As described in Example 1, a cured antirust layer was produced on a zinc-coated and chromatized steel sheet. The coating compound contained the following components:

- 16 pbw of the aliphatic urethane acrylate indicated in Example 1 (Syntholux®),
- 16 pbw of an aliphatic urethane acrylate (Viaktin® VTE 6171, 60 % in a cycloaliphatic ether acrylate, Servocure® RM-174),
- 1.5 pbw unsaturated phosphoric acid ester (Ebecryl® 168, UCB Chemicals, Belgium);
- 0.75 pbw of a trimethoxysilane derivative (Addid® 900, Wacker-Chemie),

- | | | |
|-------|-----|--|
| 2 | pbw | corrosion inhibitor
(Irgacor [®] 153, Ciba-Geigy), |
| 37.75 | pbw | Lonzamon [®] AAEMA, |
| 15 | pbw | iron phosphide as in Example 1, |
| 5.5 | pbw | Irgacure [®] 1850, and |
| 5.5 | pbw | Irgacure [®] 184. |

Upon coating and curing as in Example 1, a corrosion-protected steel sheet with similar properties as in this example was obtained.

Example 3

The procedure was as in Example 1, but there was used a coating compound of the following composition:

- | | | |
|------|-----|---|
| 20 | pbw | of an acrylic ester of an aromatic epoxy resin (Laromer® LR 8986, BASF AG), |
| 20 | pbw | of the aliphatic urethane acrylate indicated in Example 2 (Viak-tin® VTE 6171), |
| 0.5 | pbw | of a polyether-modified polydimethyl siloxane (Byk® 333, Byk Chemicals), |
| 0.1 | pbw | of a polysiloxane (Dow Corning 163 Additive, Dow Corning Corp., USA), |
| 20.6 | pbw | Lonzamon® AAEMA, |
| 10 | pbw | Magnetschwarz® S 0045, |
| 15 | pbw | Ferrophos® HRS 2132, |

- 3.8 pbw K-White[®] 105,
- 2 pbw Irgacure[®] 1850, and
- 8 pbw Irgacure[®] 184.

The coating had a thickness of 4 μ m. Irradiation was effected in air with the same light source as in Example 1. The rate of passage was 4 m/min. Substantially the same results were achieved as in Example 1.

Example 4

The procedure was as in Example 1, but the coating mixture was replaced by the following mixture:

- 22 pbw of an aromatic epoxy resin esterified with acrylic acid (Viaktin[®] EP 86, 75 % in tripropylene glycol diacrylate, Vianova),
- 10 pbw Viaktin[®] VTE 6171, as in Example 2,
- 0.5 pbw Byk[®] 333,
- 0.05 pbw of a silicone-free surface-active polymer (Byk[®] 053),
- 27.45 pbw Lonzamon[®] AAEMA,
- 8 pbw Magnetschwarz[®] S 0045,
- 12 pbw Ferrophos[®] HRS 2132,
- 3 pbw K-White[®] 105
- 1 pbw Irgacure[®] 1850, and
- 16 pbw Irgacure[®] 184.

The results were similar to those in the preceding examples.

Example 5

The procedure was as in Example 1, but coating was performed with the following mixture:

- 17 pbw Laromer® LR 9896,
- 17 pbw Viaktin® VTE 6171,
- 0.5 pbw Byk® 333,
- 0.1 pbw Dow Corning 163 Additive,
- 22.9 pbw Lonzamon® AAEMA,
- 8 pbw Magnetschwarz® S 0045,
- 17 pbw Ferrophos® HRS 2132,
- 3.5 pbw K-White® 105,
- 2 pbw Irgacure® 1850, and
- 12 pbw Irgacure® 184.

The results were comparable to those obtained in Example 1.

Example 6

The procedure was as in Example 1, but coating was performed with the following mixture:

- 19 pbw of a novolak epoxy resin cross-linked with acrylic acid,
(Ebecryl[®] 639 of UCB Chemicals, Belgium, containing 60 %
epoxy resin, 30 % trimethylolpropane triacrylate and 10 % hy-
droxyethyl methacrylate),
- 8 pbw of an aliphatic urethane acrylate
(Ebecryl[®] IRR 351, UCB Chemicals),
- 5.5 pbw Syntholux[®] DRB 227,
- 3 pbw of an unsaturated phosphoric acid ester
(Additol[®] VXL 6219, Vianova Resins)
- 0.5 pbw Byk[®] 333,
- 0.02 pbw Dow Corning 163,
- 0.4 pbw Irgacure[®] 153,
- 8,5 pbw Magnetschwarz[®] S 0045,
- 13.5 pbw Ferrophos[®] HRS 2132,
- 3.5 pbw K-White[®] 105,
- 13 pbw Irgacure[®] 184,
- 3.25 pbw Irgacure[®] 651,
- 1 pbw Irgacure[®] 1850,
- 20.83 pbw of a hydroxypropyl methacrylate
(Bisomer[®] HPMA, BP Chemicals, Buckingham, GB).

The results were comparable to those obtained in Example 1.

AMENDED CLAIMS

[received by the International Office on 31 October 2000 (31/10/00);
original claims 1-13 replaced by new claims 1-15; (3 pages)]

1. A coating mixture with anticorrosive properties, comprising a polymeric organic binder, a low-molecular liquid compound to be subjected to free-radical polymerization, a compound forming radicals under the influence of actinic radiation, and a conductive inorganic pigment, from the group including oxides, phosphates and phosphides of iron and aluminum and graphite-mica pigments.
2. The mixture as claimed in claim 1, characterized in that the conductive inorganic pigment is magnetizable iron oxide or iron phosphide or a combination of these two pigments.
3. The mixture as claimed in claim 1 or 2, characterized in that the binder is present in an amount of 15 to 60, preferably 20 to 50, in particular 20 to 40 % by weight,
the polymerizable compound is present in an amount of 24 to 60, preferably 20 to 55, in particular 25 to 50 % by weight,
the pigment is present in an amount of 10 to 40, preferably 10 to 35, in particular 12 to 35 % by weight,
and the photoinitiator is present in an amount of 5 to 30, preferably 8 to 25, in particular 8 to 20 % by weight, as well as further additives are present in an amount of 0.1 to 5, preferably 0.3 to 4, particularly preferably 0.4 to 3 % by weight.
4. The mixture as claimed in any of claims 1 to 3, characterized in that it is free of organic solvents and water.
5. The mixture as claimed in any of claims 1 to 4, characterized in that the binder itself still contains polymerizable groups.
6. The mixture as claimed in any of claims 1 to 5, characterized in that the binder is selected from the group including condensation resins, epoxy res-

ins, poly(meth)acrylates, polyurethanes, polyesters and polyethers, preferably epoxidized novolaks, bisphenol epichlorohydrin condensation products and esterification products of these resins or polymers with (meth)acrylic acid.

7. The mixture as claimed in any of claims 1 to 6, characterized in that the compound to be subjected to free-radical polymerization is a mixture of compounds, at least part of which contains more than one polymerizable group in the molecule or completely consists of the same.
8. The mixture as claimed in claim 7, characterized in that the compound to be subjected to free-radical polymerization is an ester of an α,β -unsaturated carboxylic acid, preferably acrylic or methacrylic acid, with a divalent or polyvalent monomeric or oligomeric alcohol.
9. The mixture as claimed in claim 8, characterized in that the compound to be subjected to free-radical polymerization is selected from the group including dipropylene and tripropylene glycol di(meth)acrylate, 2-acetoacetyloxy ethyl methacrylate, hexanediol diacrylate, hydroxypropyl methacrylate, hydroxyethyl methacrylate and trimethylolpropane triacrylate.
10. The mixture as claimed in any of claims 1 to 9, characterized in that the compound forming radicals upon irradiation is an aromatic keto compound.
11. A method of applying a slidable anticorrosive layer to a metallic substrate, characterized in that a mixture as claimed in any of claims 1 to 10 is applied to the surface of a metallic substrate and the coating applied is irradiated with actinic radiation of such an intensity and for such a period that a firm, hard, tough, corrosion-resistant layer is formed.
12. The method as claimed in claim 11, characterized in that the coating mixture is applied to obtain a layer thickness of 2 to 8 μm , preferably 3 to 7 μm .
13. The method as claimed in claim 11 or 12, characterized in that the substrate to be coated is a steel sheet which has previously been zinc-coated and/or chromated or has been pretreated free of chromate.

14. The method as claimed in any of claims 10 to 13, characterized in that coating and curing are effected continuously one after the other in one step and the layer cured by radiation is possibly postcured thermally.
15. A flexible metal sheet which is electrolytically zinc-coated or hot-dip coated and/or chromatised or pretreated free of chromate and has an organic layer applied thereto, which layer can be obtained by the method as claimed in any of claims 11 to 14.

[illegible]

DECLARATION/POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

COATING METHOD AND COATING MIXTURE

the specification of which:

() is attached hereto.

(X) was filed on November 29, 2001 as U.S. Serial No. 09/980,182

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

<u>199 25 631.4</u>	<u>Germany</u>	<u>04 June 1999</u>	<u>Yes (X) No ()</u>
(Number)	(Country)	(Day/Month/Year Filed)	Priority Claimed

U.S. Priority Applications

I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of the application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, Section 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, Section §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

<u>PCT/EP00/05122</u>	<u>June 5, 2000</u>	<u>Pending</u>
(Applic. Serial No.)	(Filing Date)	(Status patented/pending/abandoned)

(Applic. Serial No.)

(Filing Date)

(Status patented/pending/abandoned)

Power of Attorney

8 I hereby appoint the following attorneys to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: John E. Lynch, Reg. No. 20,940; Peter F. Felfe, Reg. No. 20,297; Norman D. Hanson, Reg. No. 30,946; John A. Bauer, Reg. No. 32,554; James Zubok, Reg. No. 38,671; James R. Crawford, Reg. No. 39,155; Andrew Im, Reg. No. 40,657, and David Rubin, Reg. No. 40,314 my attorneys with full power of substitution and revocation. Address all telephone calls to James R. Crawford, (212) 318-3148. Address all correspondence to James R. Crawford, Esq. at

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

(1) Georg GROS

Full Name/Sole or First Inventor

Signature

Date

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